

N 7 3 3 2 9 0 6

THE UNIVERSITY OF ALABAMA

FINAL REPORT

TO THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
ON GRANT NUMBER NGL-01-002-064 IN SUPPORT OF
RESEARCH IN THE AEROSPACE PHYSICAL SCIENCES

March 1, 1969 to August 31, 1973

**CASE FILE
COPY**

September, 1973

THE UNIVERSITY OF ALABAMA

FINAL REPORT

TO THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION ^{NSG}
ON NGL-01-002-064 IN SUPPORT OF RESEARCH ^{TR381}
IN THE AEROSPACE PHYSICAL SCIENCES ^{LSP}

Expiration Date: August 31, 1973 ^{CR}

Previously, The University of Alabama has submitted to NASA a Final Report on NSG-381 and NGL -01-002-001. Semi-annual reports on NGL-01-002-064 using the SIE Abstracts Reporting System and many reprints and preprints of research papers evolving from this research program have also been submitted. These reports are considered to be an integral part of this final report.

September 1973

TABLE OF CONTENTS

	Page
ABSTRACT	i
NARRATIVE	ii
I. Statistical Information	
A. The number of faculty supported under the Grant	1
B. The number of students who received support	1
C. The number of disciplines or departments involved	1
D. The number of students supported who received doctoral degrees	1
E. The number of students supported who received master's degrees	1
F. The number of papers resulting from this support.	1
II. Titles of Research Projects Supported Under this Grant, with Principal Investigators and Period of Support	
	2
III. Summaries of Research Projects Including References to Publications	
	3
IV. Financial Information	
	26

ABSTRACT

NASA Grant NGL 01-002-064 and Supplement No. 1 have provided support in the amount of \$150,000.00 for research and instruction in the aerospace physical sciences to The University of Alabama during the period September 1, 1969 to August 31, 1973. Partly as a result of these grants, the University has been able to initiate or expand its research efforts in various areas including dynamics of thin films, polymer chemistry, mechanical and chemical properties of materials, radar systemengineering, stabilization of lasers, and radiation damage of organic crystals. Brief summary reports of research accomplished and literature citations are included in the body of this report.

Robert N. Whitehurst
Professor of Physics
Principal Investigator

NARRATIVE

NASA Grant NGL 01-002-064 to The University of Alabama continued support which was begun with Grant NSG 381 and Grant NGL 01-002-001. Support furnished by these Grants has enabled the University to make considerable progress toward the goals outlined in its original Application of December 12, 1962:

- A. To enable The University of Alabama to provide increased research support in the aerospace physical sciences to the National Aeronautics and Space Administration.
- B. To educate scientists and engineers in the aerospace sciences through their active involvement in research, as graduate students and postdoctoral researchers.
- C. To facilitate the development of instructional programs in science and engineering at The University of Alabama, in particular the development of a master's degree program in Huntsville.

With the aid of these Grants, the offerings of the University at its Huntsville Campus were expanded to the point at which academic separation of the two campuses appeared desirable; graduate programs leading to the M. S. degree were offered in five different areas, and the Ph. D. degree was offered in engineering and physics. As a result of the separation, separate Applications were made to NASA for continued support under the Sustaining Universities Program,

and the Application of The University of Alabama resulted in the award in 1969 of Grant NGL 01-002-064 and, in 1970, of Supplement No. 1 to this Grant.

The Steering Committee, charged with overall direction of the research supported under this Grant, had earlier determined that the University could best fulfill its commitments to NASA by contracting its efforts in two broad fields of effort: Electromagnetics and Materials. This policy was carried over into the research program supported under NGL 01-002-064, and only research projects in these areas were considered for support. At the same time, increased efforts were made to encourage cooperation among various disciplines in their research efforts. A further judgment was that, in view of the impending end of support under the Sustaining Universities Program, more immediate benefit would result from continuing to support productive existing projects than from initiating new projects which would not have time to reach full fruition. As a result, only two new projects were initiated during the period of support under this Grant.

This Grant has had a considerable impact upon the research programs in the aerospace physical sciences at The University of Alabama. Partly as a result of the Grant, the University has initiated, and is continuing, research programs in the dynamics of thin films, polymer chemistry, mechanical properties of polymeric and composite materials, radar system engineering, wave propagation

in turbulent media, stabilization of lasers, and radiation damage of organic crystals.

Almost none of the support has been expended for equipment, which has been provided by the University or obtained from other sources. The support has primarily provided research time for faculty members and support for graduate students and research associates. Without the support provided by the Grant, many of the programs mentioned would not have been initiated or would have shown much less progress and several excellent graduate students would have been unable to further their educations at this institution.

I. Statistical Information

- A. The number of faculty supported under the Grant-----9
- B. The number of students who received support-----14
- C. The number of disciplines or departments involved-----5
- D. The number of students supported who received
doctoral degrees-----4
- E. The number of students supported who received
master's degrees-----4
- F. The number of papers resulting from this support-----13*

* Other papers are forthcoming and will be forwarded upon publication.

II. Research Projects Supported Under this Grant, with Principal Investigators and Period of Support.

- A. Studies on the Properties of Thin Anodic Oxide Films (Dr. James H. Bartlett, Department of Physics, 1 Sept. 1969-31 May 1970).
- B. Studies of the Damping Capacity of Anisotropic Materials: Metallic, Ceramic, Polymeric, and Composite (Dr. C.H.T. Wilkins, Department of Chemical and Metallurgical Engineering, 1 Sept. 1969-31 Aug. 1970).
- C. A Study of the Preparation, Structural Characterization, and Decomposition Processes of High Polymers (Dr. B. W. Ponder, Department of Chemistry, 1 Sept. 1969-31 May 1972).
- D. A Variable-Polarization Radar System (Dr. Harold Mott, Department of Electrical Engineering, 1 Sept. 1969-31 Aug. 1972).
- E. Mode Control and Stabilization of Lasers (Dr. Odis P. McDuff, Department of Electrical Engineering, 1 Sept. 1969-31 May 1973).
- F. Studies of the Effect of Ionizing Radiation on Organic Solids (Dr. Chester A. Alexander, Department of Physics, 1 Sept. 1969-13 Aug. 1973).
- G. Dissipation of Mechanical Energy and Associated Heat Generation in Polymeric Materials (Dr. Thomas L. Cost, Department of Mechanical Systems Engineering, 1 Sept. 1970-31 May 1972).

III.. Summaries of Research Projects

A. STUDIES OF THE PROPERTIES OF THIN OXIDE FILMS

Project Director: Dr. James H. Bartlett, Department of Physics

This research is part of a continuing study of the process of electrical conduction through thin anodic oxide films on various materials including bismuth, iron, vanadium, and tantalum. The objectives of the study are understanding of the details of the high-field conduction mechanism and construction of a theory which better accounts for the observed characteristics of both steady-state and transient film growth.

During the period of support under this Grant efforts have been concentrated on interpretation of the transients noted when the current through an anodic oxide layer is changed suddenly from one constant value to another. The principal feature of the transient is a sudden large change in the potential difference across the layer, this potential difference decaying approximately exponentially to the uniformly increasing "steady-state" value appropriate to the new current. It appears that none of the existing theories adequately accounts for the details of the observations.

In addition to measurement of current and potential difference, film growth and characteristics have been monitored by a digitally controlled automated ellipsometer constructed in this laboratory and permitting measurement of the optical properties of the film as it grows. A device developed by one of the students engaged in

the project has been utilized for measurement of film capacitance.

Paper and Abstract Citations

James H. Bartlett, "The Experimental Study of Passive Materials,"
Electrochimica Acta, 16, 1841-1844 (1971)

Donald J. DeSmet and M. A. Hopper, "The Design of an Automatic
Ellipsometer for the Study of the Growth of Thin Films,"
Bull. Am. Phys. Soc., Series II, 15, 1326, Abstract BF 10 (1970)

Donald J. DeSmet and M. A. Hopper, "A Study of the Anodic Oxidation
of Metals Using an Automatic Ellipsometer," Bull. Am. Phys.
Soc., Series II, 15, 1327, Abstract BF 17 (1970)

Donald J. DeSmet, M. A. Hopper, and H. Ellis, "A Study of the
Anodic Oxidation of Vanadium," J. Electrochem. Soc., 118,
860-864 (1971)

Donald J. DeSmet and J. R. Neergaard, "A Study of the Temperature
Dependence of the Anodic Oxidation of Tantalum," J. Electrochem.
Soc., 118, 2136 (1971)

B. "STUDIES OF THE DAMPING CAPACITY OF ANISOTROPIC MATERIALS"

Project Director: Dr. C. H. T. Wilkins, Department of Chemical & Metallurgical Engineering

This project is a continuing investigation into the anisotropic behavior of engineering materials as reflected by relative changes in damping longitudinal, transverse, and torsional modes of vibration.

Studies of changes in damping capacity with increasing cold working alloys led to correlating these changes with progressive fatigue damage in materials. The hollow cylindrical fatigue specimens of Hastelloy H initially used proved difficult to test by means of the resonant-bar method because of complexity of specimen shape; however, definite correlations were obtained between transverse vibrational damping and progressive fatigue damage in these specimens.

We are presently using standard sheet-type tensile specimens in tension-tension fatigue cycling under constant load conditions at yield point plus ten per cent. The aluminum alloys under investigation, types 2014-T3, 2014-T6 clad, 2014-T87, 2021-T8, and 2218-T87, are of active interest to the space effort. These have been furnished by the Metallurgy Laboratory Materials Division, Marshall Space Flight Center. Present results with alloy 2021-T8 show a satisfactory correlation between increasing damping in the specimens and progressive fatigue damage. We are now in process of broadening the statistical data base to identify and minimize error effects.

C. "A STUDY OF THE PREPARATION, STRUCTURAL CHARACTERIZATION,
AND DECOMPOSITION PROCESS OF HIGH POLYMERS"

Project Director: Dr. B. W. Ponder, Department of Chemistry

The research has involved the synthesis of some polymers containing the metallocene nucleus and the subsequent investigation of these polymers for their thermal resistance properties. The general approach was to ascertain what structural features might be desirable in the polymer, and then to synthesize the necessary monomers to polymerize.

The work was concentrated into three main areas: (1) Ferrocene-Carbodiimide polymers, (2) Ferrocene-epoxide polymers, and (3) Butadienylferrocene type homopolymers and copolymers. A brief description of each of these areas of concentration with particular emphasis on results is given below:

(1) Ferrocene-Carbodiimide Polymers- 1,1'-Ferrocene-diisocyanate was synthesized by a sequence of reaction involving ferrocene dicarboxylic acid, the acid chloride, the diazide, finally the diisocyanate. This monomer was then homopolymerized using 3-methyl - 2-phenyl -3-phospholene -1-oxide as catalyst. The polymer which was obtained as a precipitate from solution, proved to be very insoluble in all organic solvents, so that a molecular weight determination was not possible. This polymer exhibited a softening point of 270° under a nitrogen atmosphere, and a decomposition point of 210° in an oxygen atmosphere.

Copolymers of 1,1' -ferrocenediisocyanate with hexamethylene-diisocyanate, toylene -2, 4-diisocyanate, methylenebis (4-phenylisocyanate) and 3,3' -dimethoxy -4,4' -diphenyldiisocyanate were also obtained. These polymers also precipitated from solution, and were very insoluble, thus precluding any molecular weight measurements. These copolymers had softening points ranging from 210° to 260° in a nitrogen atmosphere, and decomposition points of 135° to 190° in an oxygen atmosphere.

If these copolymerization reactions were interrupted by quenching with methanol, a lower molecular weight fraction was obtained upon removal of the initial solvent, washing the residue with methylene chloride, and precipitation by addition of n-hexane. The M_n of these copolymers ranged from 800 to 2100. Because of the method by which these fractions were obtained, the number average molecular weights determined for them is probably not an index of the total extent of polymerization, but rather of the solubility of the polymer product. The relatively low molecular weights of the soluble portions suggest the possibility that the molecular weight obtainable by this method is governed by the solubility of the growing polymer chain.

(2) Ferrocene-Epoxyde Polymers - several synthetic methods were investigated in attempts to synthesize the desired ferrocene-epoxide monomers needed for the polyether type polymers. The first approach was through the 1,1' -diallylferrocene, which was to

be prepared via a Freidel-Crafts reaction from ferrocene and acryloyl chloride. This was not successful due to the polymerization of the olefinic product during the work-up of the reaction mixture. Several other attempts using various modifications of starting reagents were also unsuccessful in arriving at the desired ferrocene epoxides because of oxidation problems. The reagents dimethyloxosulfonium methylide and dimethylsulfonium methylide are epoxide forming reagents, but show essentially no oxidizing properties, so it was felt that the ferrocene epoxide monomers would be readily accessible through these ylides. However, when the simple acylferrocenes such as ferrocenecarboxaldehyde, acetylferrocene, and benzoylferrocene were treated with these ylides, the major products were aldehydes, the products of regiospecific epoxide ring opening. For example, the reaction of ferrocenecarboxaldehyde with dimethyloxosulfonium methylide gave ferrocenacetaldehyde and not vinylferrocene epoxide as the major product. The yield of the aldehyde was 64%, and none of the ketone, which would result from the alternate direction of ring opening, was detected. Under the same conditions, acetylferrocene gave rise to 2-ferrocenylpropionaldehyde in 70% yield. Ferrocenylphenylacetaldehyde was obtained in 72% yield from benzoylferrocene. These products may be explained by assuming the intermediate formation of the epoxide, followed by regiospecific ring opening and hydride shift to give the aldehyde. Since this work confirmed

the fact that ferrocene epoxides are unstable toward ring opening, the work toward ferrocene epoxide polymers was stopped at this stage.

(3) Butadienylferrocene Type Homopolymers and Copolymers-

In many polymer applications, a controlled amount of crosslinking of polymer chains is desirable after the polymer forming reaction has been accomplished. The monomers such as 1-ferrocenyl -1,3-butadiene, 4-ferrocenyl -1,3-pentadiene and 1-phenyl -1,3-butadiene have the potential of undergoing vinyl addition copolymerization, and subsequently reacting with suitable crosslinking agents to form a crosslinked polymer by thermal treatment. The determination of reactivity ratios of monomer pairs in copolymerization reactions is of considerable importance, since the chemical composition of a copolymer depends mainly upon the relative reactivities of the two monomers toward the two intermediate radicals. In this area of study, the ferrocene monomers with conjugated side chains were not available, and methods were worked out for their synthesis. These monomers were then copolymerized with each other as well as with styrene, and their reactivity ratios determined. These reactivity ratios are listed in Table 1.

Table 1

Reactivity Ratios for Copolymerization of
Styrene (M_1) with Comonomer (M_2)

Comonomer (M_2)	r_1	r_2
1-Ferrocenyl -1,3- butadiene	0.76 \pm 0.01	0.67 \pm 0.10
1-phenyl -1,3- butadiene	0.71 \pm 0.01	0.72 \pm 0.02

Number average molecular weights were also determined on these copolymer in benzene solution. These ranged from 3,000 to 4,000.

Publications arising from the work supported by this grant:

- (1) "An Improved Synthesis of 1-Ferrocenyl -1,3-butadiene," by B. W. Ponder, R. Craig Kneisel, and Danny H. Lewis, Organic Preparations and Procedures, International, 3, 171-175 (1971).
- (2) "4-Ferrocenyl -1,3-Pentadiene," by Danny H. Lewis, Marvin C. Neal, and B. W. Ponder, Synthetic Communications, 2, 93-96 (1972).
- (3) "The Reaction of Acylferrocenes with Dimethyloxosulfonium Methylide and Dimethylsulfonium Methylide," by John P. Sevenair, Danny H. Lewis, and B. W. Ponder, J. Org. Chem., 37, 4061 (1972)
- (4) "Diimide Polymers from 1,1' -Ferrocenediisocyanate," by B. W. Ponder, John T. Bateman, and John P. Sevenair, submitted to J. Polymer Science.
- (5) "Free Radical Polymerization of 1-Ferrocenyl -1,3 butadiene and 1-Phenyl -1,3 -butadiene. Reactivity Ratios and Q and e Values," by D. H. Lewis, R. C. Kneisel, and B. W. Ponder, accepted by Macromolecules.

D. A VARIABLE-POLARIZATION RADAR SYSTEM

Project Director: Dr. Harold Mott, Department of Electrical Engineering

Description of the Work

The investigations carried out in this area during the Grant period were divided into two parts. In the first part a variable-polarization system previously developed at The University of Alabama was used to make extensive measurements at X-band of backscattering from models as a function of polarization of the transmitted wave. The polarization used changed from linear vertical, through elliptical with vertical major axis, through circular, through elliptical with horizontal major axis, and finally to linear horizontal. The receiving system maintained the same polarization characteristics as the transmitter. The results showed that received power can be affected very strongly by varying the polarization of the system.

The second problem was a theoretical study of the polarization changes introduced into a wave by transmission through a turbulent atmosphere. This work was concerned with a beam wave of Gaussian intensity distribution and arbitrary divergence propagating in a turbulent medium characterized by a Kolmogorov spectrum. A mean-square depolarization fluctuation was obtained which reduced to the simpler forms determined by other investigators

when we took the special case of a collimated beam wave or the plane wave case. The results show that off the beam axis the depolarization can be greater than for the plane wave, and that near the beam focal point the depolarization may decrease by orders of magnitude.

Publications

The work performed under this Grant was reported in the following publications:

"Mean-Square Depolarization of an Uncollimated Beam Wave in a Turbulent Medium," Feng-cheng Chang, Harold Mott, and W. E. Webb, IEEE G-AP International Symposium Digest, pp. 355-358, December 1972.

"Mean-Square Depolarization of an Uncollimated Beam Wave in a Turbulent Medium," Feng-cheng Chang, Harold Mott, and W. E. Webb, URSI Abstracts, p. 31, December, 1972.

"Depolarization of an Uncollimated Laser Beam in a Turbulent Medium," Feng-cheng Chang, Harold Mott, and W. E. Webb, accepted for publication by Journal of the Franklin Institute.

E. MODE CONTROL AND STABILIZATION OF LASERS

Project Director: Dr. Odis P. McDuff, Department of Electrical Engineering

Introduction

The basic requirement of an optical communication system is the provision of a satisfactory source of energy. If modern heterodyne techniques are to be used so that full advantage of the laser's high frequency can be taken, the temporal coherence requirements placed upon the laser dictate that it be frequency stabilized.

Non-collinear or ring lasers are known to produce an output which can be used to measure the laser rotation rate about an axis perpendicular to the plane of the ring. Other characteristics of the ring laser, such as the dependence of its output frequency upon deflections of the beam internal to the cavity, promise potential applications.

The research included in this report has included both of these topics--frequency stabilization of a straight-cavity laser and unique characteristics of ring lasers.

The latter phase of the work was terminated at an early stage because of budget limitations.

Technical Summary

Single Mode Laser

A single mode laser with an intracavity modulator was

analyzed numerically using the digital computer. This involved the solution of nonlinear, coupled-mode differential equations and showed the existence of a discriminant which tells when the laser oscillating frequency departs from the frequency of the atomic line center of the medium (see reference (1) above). The numerical study reported in detail in reference (4) showed the range of parameters and their optimum values for such operation. It was found that loss modulation tried by others would give very poor results compared to phase modulation. The equations were linearized and approximate equations derived which could be used to predict the system performance without resorting to numerical studies.

A high-gain flowing-gas CO₂ laser was constructed as a subject for experimental studies. The laser had a discharge tube approximately 50 cm long with NaCl Brewster windows at each end. Silicon and germanium-coated mirrors were used in the 1 meter long optical cavity. A high speed gold-doped germanium photo detector and a power meter were used in testing the laser. A multimode power output of about 5 watts was obtained.

A gallium-arsenide electrooptic modulator was designed and constructed for the intracavity modulation. The crystal was .5 cm X .5 cm X 5 cm and performed according to

theoretical expectations. By changing the rf circuitry, the modulator was pulsed on and off and a synchronous detection scheme used to eliminate spurious signals.

The laser was modulated both externally and internally and the characteristics compared to the theoretically expected results.

Because of the limitations of the available photo detector, it was impossible to observe directly the rf beat-note expected in the output (all the equipment was obtained from non-contract funds and/or borrowed) and, thus, it was necessary to rely on other evidence to verify the mode-locked behavior. The other evidence, such as variation of laser average power as the phase modulator was pulsed on, indicated that mode-locking was successfully obtained. The various experimental curves that were obtainable with the equipment at hand all compared favorably with the expected curves. Thus, it is felt that, with a fast enough detector, the stabilization scheme being considered is quite feasible. Such detectors are available but it was not feasible to purchase one for this work because of fund limitations.

Ring Laser

A helium-neon ring laser was constructed using an

available commercial high gain laser. A KDP modulator was designed and constructed and used for intracavity modulation of the ring laser. This work, reported in detail in reference (3) showed that mode-locked pulsing and frequency modulation were possible in a phase-modulated ring laser. Several follow-up projects had to be abandoned because of lack of funds.

Summary

The principal goals of the research were achieved. It was demonstrated that phase-locking of a single-mode laser could be obtained and, by inference, that a discriminant could be obtained which was useable for stabilization purposes. The work was restricted considerably by the lack of some rather expensive components which were needed.

Published Results

The following publications and reports have resulted from the research:

1. Odis P. McDuff and Richard A. Curtis, "Stabilization of Single Mode Lasers Using Intracavity Perturbation," Conference Record, 1968 IEEE Region III Convention, pp. 5.3.1-5.3.7. April, 1968.
2. Odis P. McDuff and Richard A. Curtis, "Stabilization of a Phase Modulated, Mode Locked, Single Mode Laser," Digest of Technical Papers, 1968 International Quantum Electronics Conference, p. 57, May 1968.
3. Charles M. Hess, "Internal Phase Modulation of Ring

Lasers," M.S.E.E. thesis, University of Alabama, 1971.

4. Richard A. Curtis, "Stabilization of Single Mode Lasers Using an Intracavity Perturbation," M.S.E.E. thesis, University of Alabama, 1969.

In addition, part of the work included in this research was reported in a chapter entitled, "Techniques of the Gas Lasers," which was authored by Dr. Odis P. McDuff and which appeared in The Laser Handbook, pp. 631-702, published by North Holland Publishing Company in 1973. *A. ip*

F. AN ESR STUDY OF THE EFFECTS OF X-IRRADIATION ON SINGLE CRYSTALS OF CYTIDINE

Project Director: Dr. Chester Alexander, Jr., Department of Physics

a. Experimental and Theoretical Studies of Crystals

1. Cytidine

A number of single crystals of cytidine have been grown from water-alcohol solutions. From published crystal structure data a determination of the c-crystal axis was made. The other two crystal axes were determined by x-ray diffraction techniques.

Professor Atwood of The University of Alabama, Department of Chemistry allowed us to use his diffraction equipment and helped us interpret our results.

Single crystal samples were x-irradiated and studied with ESR and ENDOR techniques. These measurements were made on a K-band ESR spectrometer we constructed and which we later modified to allow ENDOR measurements to be made also. Experiments were carried out at room temperature (ESR and ENDOR) and at 77°K (ESR). Because of the changing nature of the room temperature radical species in the irradiated crystals, ESR and ENDOR spectra were recorded immediately after irradiation and then at regular intervals for a period of weeks and finally

after a period of one year. In the case of crystals irradiated at 77°K, ESR spectra were taken immediately after irradiation and then after warming to room temperature.

A preliminary ENDOR spectrum of our irradiated crystal was taken at Emory University by Professor A. K. Garrison, but the results of this study were not conclusive. We modified our ESR spectrometer and used borrowed equipment to make ENDOR measurements at K-band microwave frequencies at room temperature. After the Department of Physics purchased equipment for these experiments we also were able to make double-ENDOR measurements on these crystals. To our knowledge these types of ENDOR measurements under these conditions have not been previously reported in the literature.

Simple Huckel and Extended-Huckel molecular orbital calculations were carried out to give theoretical values for unpaired electron densities resulting from radicals in the ribose sugar group. These theoretical results were compared to our experimental results to help determine the nature of radical species.

As a result of these studies on cytidine crystals we have determined radical models for two radical species in irradiated cytidine.

(a) Our results show that the initial room temperature radical in irradiated cytidine is an unpaired electron coupled to three different hydrogen nuclei: The g-factor tensor determined from ESR data and three hyperfine tensors determined from ENDOR data aid in determining which particular hydrogen atoms in the cytidine molecule couple to the unpaired electron. The radical is formed in the ribose sugar group of the molecule. A paper describing our results has been published (*J. Chem. Phys.* 58, 4891 (1973)).

(b) A stable radical species in cytidine has been determined as an unpaired electron coupling to one hydrogen nucleus. Our results indicate that the radical is formed in the ribose sugar group of the cytidine molecule. The coupling hydrogen atom is in a β -position with respect to the orbital containing the unpaired electron. Preliminary results of this study were reported at a meeting of the American Physical Society and additional details

are given in the dissertation of D. L. Allison (summer 1973). A paper describing these results will be submitted for publication in the near future.

2. Methyl Mercaptapurine Ribose (MeMPR)

Single crystals of MeMPR were grown and irradiated with x-rays. ESR and ENDOR techniques were used to study the radicals formed in the crystals. Two radical species have been formed, one due to abstraction of a methyl group and one due to a hydrogen addition reaction. The large g-factor variation of the ESR spectra of one radical indicated a large spin density localized on a sulphur atom, while the ENDOR data indicated a hydrogen atom added to the purine base in the other radical. Preliminary results of these experiments were reported at a meeting of the Americal Physical Society.

3. Neodymium Bromide

We have grown single crystals of neodymium bromide hexahydrate and we are studying the ESR spectra from non-irradiated samples. We have compared the ESR spectra taken at room temperature with spectra obtained at 77°K. Using these data we can obtain information about the crystal field parameters of

this compound. We expect to publish these results when they are completed.

b. Experimental Apparatus

1. A cold finger dewar and a special type microwave cavity were designed and constructed for our low temperature ESR measurements. The new cavity and dewar design allow x-irradiation and ESR observations of crystals at temperatures from 60 K to room temperature. A temperature controller and heater used with the dewar allow variable temperature studies to be carried out. A paper describing our dewar was presented at the Southeastern Magnetic Resonance Conference in October, 1970.

2. We have designed and built a device which converts a sweeping frequency signal from a tracking NMR oscillator or rf oscillator to a sweep voltage for an x-y recorder. This device will produce an 0-10V analog output for magnetic field sweeps of 100, 250, 500 or 1000 gauss or for frequency sweeps of 1, 2.5, 5 or 10 MHZ. The device also makes it possible to start a sweep and zero the x-axis of the x-y recorder at any field or frequency value. This device is very useful for making ESR and ENDOR measurements. A paper

describing this device will be submitted for publication in the near future.

c. Paper and Abstract Citations

ENDOR and ESR Studies of Irradiated Cytidine, Don A.

Hampton and Chester Alexander, Jr., J. Chem. Phys. 58,

4891 (1973).

A Cold Finger Dewar for X-Irradiation and ESR Observations of Crystals at 80°K, Chester Alexander, Jr., and

Don A. Hampton, Abstracts of the 2nd Southeastern Magnetic Resonance Conference, Oct. 1970.

ENDOR and ESR Studies of A Stable Radical in Irradiated Cytidine, D. L. Allison and Chester Alexander, Jr.,

Bull. Am. Phys. Soc. 18, 252 (1973).

ESR and ENDOR Studies of Irradiated 6-methyl Mercaptopurine Riboside (MeMPR) Single Crystals, H. L. Pugh and C. Alexander, Jr., Bull. Am. Phys. Soc. 18, 410 (1973).

G. DISSIPATION OF MECHANICAL ENERGY AND ASSOCIATED HEAT GENERATION IN POLYMERIC MATERIALS

Project Director: Dr. Thomas L. Cost, Department of Mechanical Systems Engineering

I. Research Summary

Objective: The objective of this project was to develop an adequate theory and computational ability for predicting the heat generated in solid polymeric materials as a result of sustained mechanical vibratory motion.

Background: Viscoelastic materials are being used to significant and increasing degree in applications for which cyclic loads are important. For example, such items as gears, bellows, mechanical couplings, tubing, bearing pads and vibration absorbers are commonly made from plastic-type materials and used in vibration environments. Also, solid propellants, aerospace vehicle structural components, tires, etc. are manufactured from rubbery or fiberglass type materials which can be described as viscoelastic. The problem of heat generation in these materials is one which has not been studied significantly in the past.

The problems associated with heat generation can be significant. The problem of heat generation in tires as a result of flexing is probably more commonly known than others. In general, the heat generated in these materials affects the strength and stiffness of the material since the mechanical properties of viscoelastic materials are strongly dependent on temperature. Such changes in

strength and stiffness can affect the structural integrity of structures constructed of viscoelastic or polymeric materials. Also, certain solid propellants possess chemical instabilities which are strongly temperature dependent and which can lead to catastrophic failures of solid propellant rocket motors.

Another problem associated with this phenomenon is that of fatigue failures in polymeric materials. Since a large amount of heat is generated in the sample in a fatigue test, some account must be made of the effect of fatigue strength on sample temperature.

Research Results: Efforts devoted to this project have produced a theory for predicting the energy dissipated in composites subjected to cyclic loading which has been developed and applied to the problem of a circular rod of a particulate composite subjected to a uniaxial cyclic load on one end while fixed at the other. The circular rod problem was selected because of the ease with which experiments might be conducted and because of the one-dimensional nature of the boundary value problem to be solved analytically. The theory has been included in a computer program which determines the effect of cyclic heating on the structural response of the rod. General thermal boundary conditions are included. A finite-difference numerical technique was used to obtain the analytical solution to the problem.

Experiments were conducted on uniaxial rods of a polyurethane material called Solithane and comparisons made between analytical

and experimental results. The comparisons indicate the theory is adequate and suitable for applying to more complex problems which might involve more complicated geometrical shapes and material property behavior. The finite difference computer solution technique appeared inadequate, however, to handle more complicated geometries. Consequently, a finite-element computer solution was developed for this problem and found to give favorable results. The finite-element method was also determined to be easily adaptable to more complex geometrical shapes.

In summary, both an adequate theory for predicting the heat generated in polymeric materials as a result of infinitesimal periodic mechanical vibrations and a computational procedure for applying this theory to complex geometries has been developed. The results are immediately applicable to more complex cases. The research results have been described in the open literature as described in Section II, Publications.

II. Publications and Presentations

The research results obtained on this project have been described in detail in the following publications and presentations.

Publications

"Thermomechanical Dissipation Analysis of Thermoviscoelastic Solids by Finite Elements," Thomas L. Cost, in Developments in Theoretical and Applied Mechanics, Vol. 6, 1972, Sixth Southeastern Conference on Theoretical and Applied Mechanics, edited by E. G. Henneke and S. C. Kranc, pp. 727-759.

Presentations

- 1) "Thermomechanical Dissipation Analysis of Thermoviscoelastic Solids by Finite Elements," presented at the Sixth South-eastern Conference on Theoretical and Applied Mechanics, Tampa, Florida, March, 1972.
- 2) "Heat Generation and Structural Integrity Effects in Viscoelastic Solids," presented at the Mid-South Meeting of the Society for Experimental Stress Analysis, Huntsville, Alabama, July, 1972.

FINANCIAL INFORMATION

NGL-01-002-064

Grant Began: March 1, 1969
Grant Expired: August 31, 1973

March 1, 1969 - February 28, 1970	\$ 35,000.00
March 1, 1970 - February 28, 1971	45,000.00
March 1, 1971 - February 29, 1972	45,000.00
March 1, 1973 - August 31, 1973	<u>25,000.00</u>
TOTAL	150,000.00*

*The above includes Supplement No. 1.